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Laser-induced breakdown spectroscopy: flat surface *vs*. cavity structures†

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Cavity formation is a common phenomenon involved in solid-state analysis when repetitive laser pulses are applied to induce breakdown spectra. While previous LIBS investigations have been mostly focused on laser ablation on flat surfaces, the development of a laser-induced plasma inside cavity structures is of both fundamental and practical significance for quantitative chemical analysis using LIBS. In this paper, we attempt to answer the question, to what extent cavity formation would influence the temperature and electron density of laser-induced plasma. We found a significant effect of cavity aspect ratio on plasma characteristics, in particular, the measured high temperature and electron density of laser-induced plasma inside cavity structures.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a powerful tool for solid-state chemical analysis, for example, elemental depth profiling and spatial heterogeneity characterization. At laser intensities typically used for LIBS analysis, coupling of intense electromagnetic energy with a solid sample results in melting, vaporization, and ejection of atoms, ions, and molecular species.[1] As a consequence, cavity structure, characterized by its depth-to-diameter ratio (the aspect ratio), develops when the same sample location is irradiated with repetitive laser pulses. The resulting LIBS is therefore associated with laser interactions with the cavity structure of the sample, rather than a flat surface. The scope of this research was to investigate fundamental LIBS characteristics inside cavity structures, and to compare properties of laser-induced plasmas developed inside and outside cavities of different aspect ratios.

Previous theoretical radiation analysis[2] indicated that the amount of energy absorbed by a cavity would increase with increasing aspect ratio. For instance, with an aspect ratio of 5, the amount of energy absorbed by the cavity could differ by one order of magnitude from the flat surface case. Numerical calculations[3] also suggested how a large amount of the reflected laser beam inside the cavity could enhance the energy coupling between the laser beam and the sample. For chemical analysis applications, the cavity aspect ratio was found[4] to be an important parameter affecting the degree of elemental fractionation, a process in which the elements are selectively ablated with the ionized sample mass (plasma) having a different chemical composition from that of the unperturbed sample. Despite theoretical implications of increased laser energy coupling to a solid sample when high aspect ratio cavities are present, the fundamental processes of laser interactions with a cavity structure remain unexplored.

2. Experiments

Fused silica glass was the sample material in this study and the silicon emission lines were measured to determine the laser-induced plasma properties (temperature and electron number density). Cavities of different diameters and depths were fabricated, before LIBS experiments, using a commercial laser micro machining workstation. The LIBS experimental system included a quadrupled Nd:YAG laser operating at 266 nm with a 3 ns pulse duration. The laser beam was focused onto the target to a 50 μ spot diameter using a quartz lens. A second lens was used to image the laser-induced plasma into the entrance slit of a spectrometer. The emission spectra were detected by an Intensified Charge-Coupled Device (ICCD) system consisting of a thermoelectrically cooled CCD with a microchannel plate image intensifier. This spectrometer and detection system has a spectral resolution of 0.1 nm. The detector gate width was 30 ns, which remains constant for all experiments. Dark current background of the CCD detector was subtracted from the measured spectral data for each measurement. Spatial distribution of plasma temperature and electron number density were determined by measuring Stark broadening of the silicon emission lines and the relative line-continuum ratio.[5] The emphasis of this study was spatially and temporally resolved measurements during the early phase (<300 ns) of the plasma generated inside cavity structures. Fig. 1 is a schematic illustration of the experimental setup.

3. Results and discussions

Fig. 2 shows the plasma spectra from laser ablation inside a 160 μ diameter, 480 μ deep cavity (Fig. 2a), compared with the plasma spectra from laser ablation on a flat surface (Fig. 2b). The laser irradiance was approximately 16 GW cm^{-2}. The silicon emission line Si(I) at 288.16 nm was used for plasma

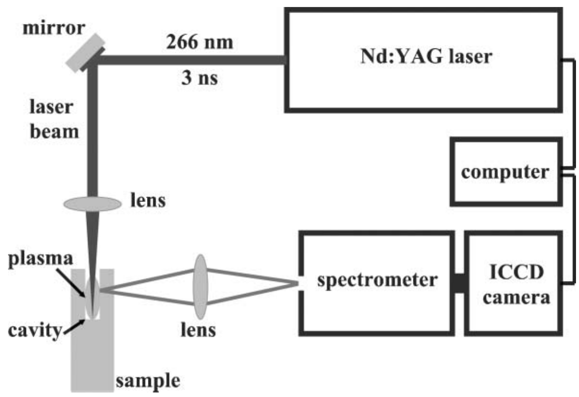

Fig. 1 Schematic illustration of LIBS setup for ablation inside a cavity structure.

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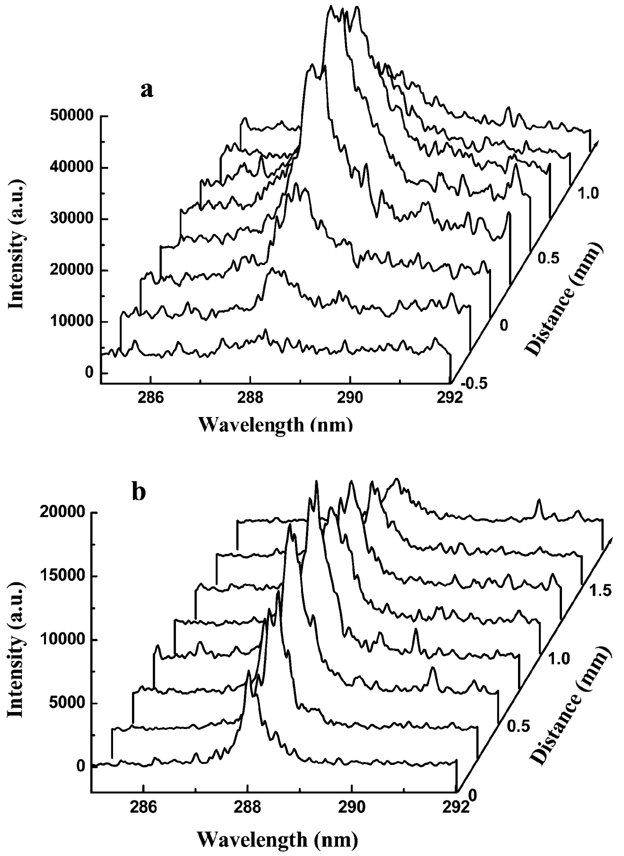

Fig. 2 (a) Spatial distribution of plasma emission from the 160 μ diameter cavity (depth 480 μ) at the center wavelength of 288.16 nm and time of 100 ns. Cavity bottom is at −0.5 mm. (b) Spatial distribution of plasma emission from the flat surface at the center wavelength of 288.16 nm and time of 100 ns.

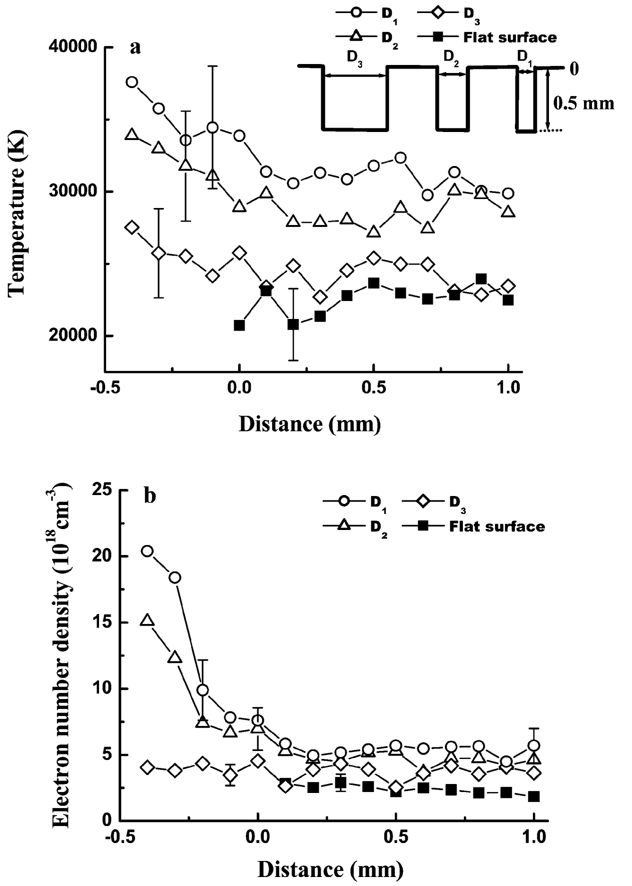

Fig. 3 (a) Plasma temperature and (b) electron number density *vs.* distance for different aspect ratio cavities (delay = 100 ns, irradiance 7.0 GW cm^{-2}). Aspect ratio = Depth/Diameter = L (μ)/D (μ). L/D_1 = 480/80 ∼ 6; L/D_2 = 480/160 ∼ 3; L/D_3 = 480/490 ∼ 1.

diagnostics. The spectra inside the cavity have a wider Full Width at Half Maximum (FWHM) as well as higher emission intensity. The position of the maximum emission intensity is at 0.9 mm from the bottom of the cavity; for flat surface results, the location of maximum emission intensity occurs at 0.6 mm above the surface.

As determined from measuring the Stark broadening of the Si emission lines and the relative line-continuum ratio, Fig. 3 shows the plasma temperatures T and electron number densities n_e for laser ablation of three cavities as well as the flat surface. These three cavities have the same depth (∼480 μ) but different diameters (80, 160, and 490 μ). The plasma temperature and electron number density are highest in the largest aspect ratio cavity. As the aspect ratio decreases, the plasma temperature and electron number density in the cavity approach the flat surface results. For the largest aspect ratio, the plasma temperature decreases from 38000 K (in the cavity) to 30000 K (1.5 mm above the cavity bottom); electron number density falls from 2×10^{19} to 5×10^{18} cm^{-3}. On a flat surface, the plasma temperature and electron number density are much lower, 20000 K and 2×10^{18} cm^{-3}, respectively, and do not change as much with distance from the surface.

These results are related to plasma confinement by the cavity walls and plasma shielding (absorption and/or reflection of the laser beam by the plasma). Once the plasma is initiated inside the cavity, its lateral expansion is confined. The cavity acts as a trap in which photon energy of the trailing edge of the laser pulse can be efficiently absorbed by the confined laser plasma. Additional electrons will be produced *via* electron-neutral, electron-ion inverse bremsstrahlung, as well as photo ionization. After the plasma is significantly ionized, electron-ion inverse bremsstrahlung dominates the absorption. Given the laser wavelength and plasma density measured, the absorption coefficient for electron-ion inverse bremsstrahlung was estimated to be ∼1 cm^{-1} at 3 ns for the cavity with aspect ratio 3.[6] The absorbed energy is converted into the internal energy of the plasma. After the completion of the laser pulse, the plasma expands out of the cavity and the plasma temperature and electron number density in the cavity decrease.

Two locations were selected for the cavity and one for the flat surface to compare plasma temperature and electron number density as a function of time (Fig. 4). Location A is inside the cavity at a height of 0.2 mm above the bottom surface, location B is outside of the cavity at a height of 0.7 mm above the bottom of the cavity. Location C is 0.2 mm above the flat surface. Location A and C are equal distance above the solid material.

An adiabatic model is often used to describe laser-induced plasma expansion.[7] For an adiabatic expansion, the expressions for plasma temperature and electron number density as a function of time are[6] $T(t) \propto t^{-2\alpha(r-1)/[\alpha(r-1)+2]}$ and $n_e(t) \propto t^{-2\alpha/[\alpha(r-1)+2]}$, respectively, where γ is the ratio of specific heat capacities at constant pressure to constant volume, and α is the dimensionality: $1 < \alpha < 3$.[7]

The plasma at location C from laser ablation on the flat surface gives: $T \propto t^{-0.54 \pm 0.04}$ and $n_e \propto t^{-0.95 \pm 0.06}$, solving for α and γ yields: $\alpha = 1.30 \pm 0.12$, $\gamma = 1.57 \pm 0.08$, respectively. The calculated values of α and γ are within experimental error to the values obtained previously.[6] The calculated dimensionality 1.30 supports preferential spatial expansion in the direction perpendicular to the target. The calculated γ value, 1.57 is close to the specific heat for an ideal gas of 5/3. Therefore, an adiabatic process can be used to describe the plasma expansion for this experiment.

For the plasma that has expanded outside of the cavity at location B: $T \propto t^{-0.52 \pm 0.03}$ and $n_e \propto t^{-0.98 \pm 0.05}$,

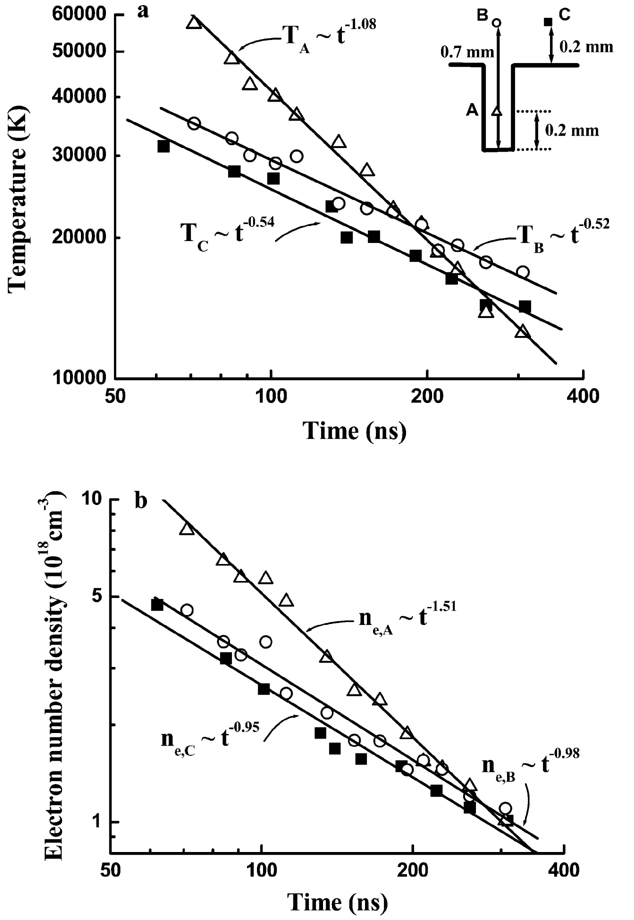

Fig. 4 Temporal evolution of plasma temperature (a) and electron number densities (b) inside and outside of the cavity. Cavity diameter is 80 μ and depth is 480 μ. Irradiance is 7.6 GW cm^{-2}. (A) Plasma inside cavity, distance d = 0.2 mm. (B) Plasma outside of cavity, d = 0.7 mm. (C) Plasma from flat surface, d = 0.2 mm.

corresponding to: α = 1.32 ± 0.09, γ = 1.53 ± 0.06, respectively, which are close to the flat surface results above. Thus, after the plasma expands out of the cavity, an adiabatic model can describe plasma temperature and electron number density variations.

For the plasma in the cavity at location A, $T \propto t^{-1.08 \pm 0.04}$ and $n_e \propto t^{-1.51 \pm 0.06}$, corresponding to α = 3.31 ± 0.17 and γ = 1.72 ± 0.05. The dimensionality value inside the cavity indicates that an adiabatic expansion model is not suitable (greater than 3). Once the plasma is generated, hydrodynamic confinement of the plasma expansion occurs in the cavity; energy from the plasma can be transferred to the walls by normal electron heat conduction, electron–ion recombination on the cavity walls, short-wavelength thermal plasma radiation, and condensation of vapor that moves to the surface due to the plasma pressure. The plasma cools rapidly by interaction with cavity walls, resulting in a sharp decrease of plasma temperature. In addition, the confinement effects may modify the shock wave propagation inside the cavity, influencing laser beam interactions with the hydrodynamic expansion of the plasma.

We also performed experiments to investigate the dependence of plasma characteristics on laser irradiance. The plasma temperature and electron number density as a function of irradiance for laser ablation inside a cavity (aspect ratio 4) and on a flat surface are given in Fig. 5. The data were obtained at a delay time 30 ns and a distance of 1 mm above the material. At each laser irradiance, the plasma temperature and electron number density are greater for ablation in the cavity. As discussed before, this is the result of plasma confinement inside the cavity.

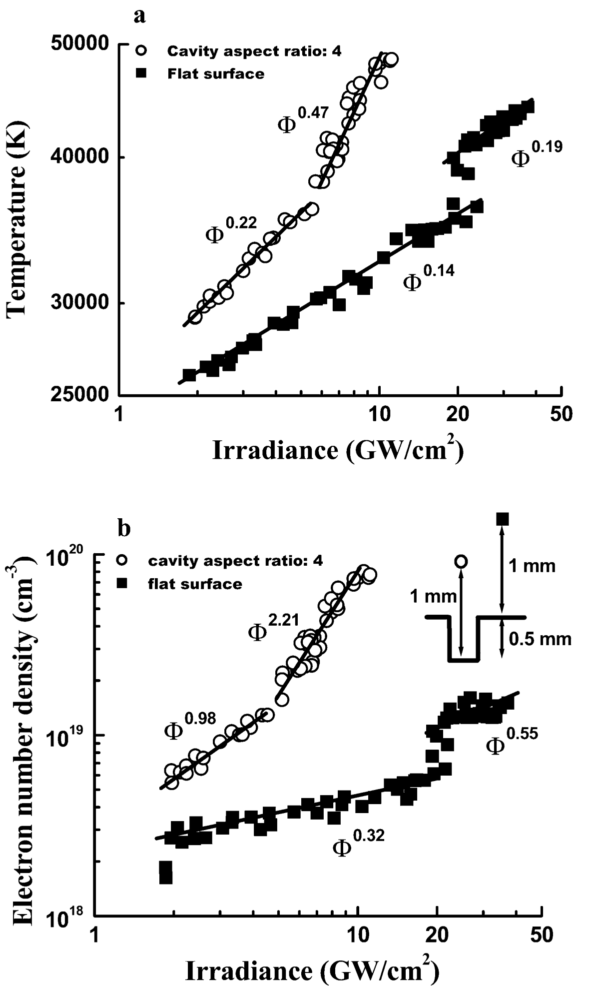

Fig. 5 (a) Plasma temperature and (b) electron number density *vs.* irradiance for laser ablation of a flat surface and a cavity (depth 500 μ, aspect ratio 4). Data were taken at 30 ns.

As shown in Fig. 5, for laser ablation of the flat surface, the plasma temperature and electron number density change dramatically at an irradiance threshold of approximately 20 GW cm^{-2}. This threshold irradiance is lower for ablation inside a cavity (~5 GW cm^{-2}). Fig. 6 shows the measured crater depth variations as a function of irradiance for laser ablation on the flat surface. The crater depth increases abruptly at the irradiance of ~20 GW cm^{-2}, the same irradiance value as that for the dramatic change of the plasma characteristics. As the laser irradiance was increased across this threshold, the crater depth changed from 1 to more than 10 μ per pulse. These data are consistent with the mechanism of phase explosion,

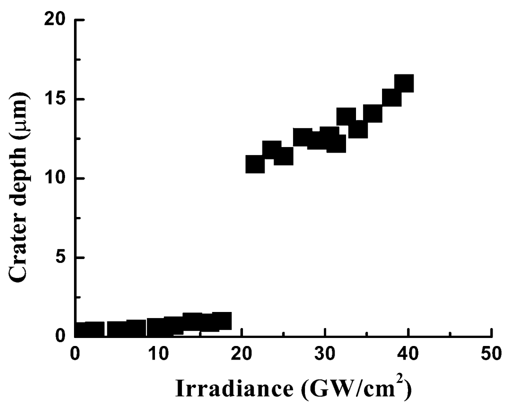

Fig. 6 Single pulse laser ablation crater depth *vs.* laser irradiance. The sample was fused silica.

which happens when the sample is heated rapidly and the molten layer becomes superheated.[8] Compared to laser ablation of a flat surface, plasma confinement results in much higher plasma temperature and electron number density inside a cavity. A plasma of very high temperature and density inside a cavity can induce self-focusing effect of the ablation laser beam, producing even stronger laser energy density at the material surface. As a consequence, phase explosion threshold is crossed at lower laser irradiance for ablation inside a cavity.

4. Conclusions

The effects of cavity formation on laser-induced plasma expansion were investigated. The temperature and electron number density of a laser-induced plasma inside a cavity were found to be greater than those outside of a cavity. As the aspect ratio decreased, the plasma temperature in the cavity approached the flat surface results. Plasma wall interactions must be considered to describe the plasma in the cavity, and explain the enhanced "rate" of decrease of temperature and electron number density with the cavity as compared to the flat surface. The adiabatic model will not be suitable to describe the laser-induced plasma inside the cavity since plasma confinement is not included in such simplified model. In addition, we observed phase explosion phenomenon for laser ablation of fused silica. Compared to ablation of a flat surface, the dramatic change of plasma temperature and electron number density occurs at lower irradiance threshold for laser ablation of cavities. The information obtained by this study of LIBS in cavity structures may help improve quantitative chemical analysis such as elemental depth profiling using laser spectra.

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